

ART. IX.—*Further Notes on the Essential Oils of Australian Myrtaceae.*

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PART I.—*The Essential Oil of Eugenia Smithii.*

By A. E. DAWKINS, B.Sc.

Eugenia smithii (N.O. Myrtaceae), commonly known as "Lilly-pilly," occurs in Eastern Australia from Victoria to Queensland. It is a magnificent evergreen ornamental tree, reaching a height of from fifty to eighty feet; the leaves are dark green, oval, slightly pointed, and covered with oil-dots; the flowers are small and pale green, and produce numerous white, lilac and mauve berries, which are very showy when fully ripe.

The wood produces a dark, close-grained timber, said to be well adapted to ornamental furnishings. Baron von Mueller records that the bark contains 17 per cent. of tannin.

Some species of the genus *Eugenia* produce large, juicy table fruits of a wholesome, agreeable flavour; the young flower-buds of *E. caryophyllata* form the spice well-known as "cloves"; "allspice" is the product of *E. pimento*; and the seeds of *E. jambolana* have been used as a remedy for diabetes.

As *Eugenia Smithii* is found in such profusion in the native state, and grows rapidly under cultivation, it was thought desirable to investigate and place on record the nature of the oil contained in its foliage.

The material from which the oil was steam-distilled was obtained from the Melbourne Botanical Gardens, through the courtesy of the Curator.

Physical Constants.

The yields and physical constants of the two samples worked with were as follow:—

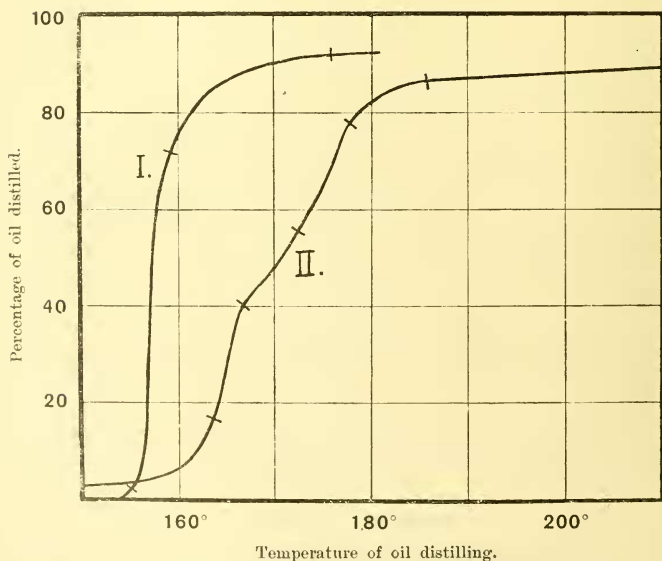
TABLE I.

Date of Distillation	- -	May, 1914	-	July, 1914
Weight of leaves in lbs.	-	148	-	165
Ounces of oil	- -	10.5	-	7.5
Percentage yield	- -	0.44	-	0.28
Specific gravity $d_{15,15}$	-	.866	-	.863
Optical rotation α_{D15}	- -	+35.0°	-	+34.6°
Refractive Index μ_{20}	-	1.4701	-	1.4675

The difference in yield illustrates the seasonal variation usually observed in the distillation of oils from the Myrtaceae, but the physical constants are so similar that the two samples may be regarded as identical in composition. The oil is pale yellow in colour and possesses a sweet penetrating odour.

Fractional Distillation.

By way of exploration 50 c.c. of the oil was submitted to a fractional distillation in a still of standard dimensions, the results of which are embodied in the graph and in Table II.



I. *Eugenia Smithii*. II. *Eucalyptus platypus*.

TABLE II.

Fraction.	Temperature of distillation.	Percentage of total by volume.	Specific gravity $d_{15,15}$	Optical rotation α_{D15}	Refractive index μ_{20}
I.	Below 155°c	1.6	—	—	1.4673
II.	155° - 159°	69.6	.860	+38.9°	1.4661
III.	159° - 176°	21.1	.877	+31.3°	1.4697
Residue	Above 176°	7.7	—	—	1.4813

The curve indicates that the oil contains one preponderating constituent, and suggests that this is probably pinene.

Chemical Examination.

a Pinene.—From a fraction boiling at about 156 deg. C. a nitrosochloride was prepared; melting point = 104-105 deg., indicating presence of *a*-pinene. The rotation of the original oil and that of the pinene fraction show that the hydrocarbon is present in the dextro form, a conclusion in agreement with the observation that the nitrosochloride was formed only with difficulty (v. Gildemeister and Hoffmann—*The Volatile Oils*, p. 296).

β Pinene.—In order to test for the presence of *β* pinene (or nopinene), which is associated with the *a*-pinene of turpentine oils, the following experiment was carried out (Wallach, *Liebs. Ann.* 356, (1907), 228):—30 c.c. of a fraction boiling between 157 deg. and 166 deg., was oxidised with excess of cold alkaline solution of potassium permanganate, the liquor was filtered from manganese dioxide, steam-distilled to remove unchanged oil, and concentrated to a third of its original bulk. There was no separation of the sparingly soluble sodium nopinate. (A control experiment using a similar fraction from oil of turpentine yielded a sodium salt, the acid set free from which had the melting point characteristic of nopinic acid.)

Phellandrene.—The presence of phellandrene and other nitrosite-forming hydrocarbons, was tested for with negative result.

Acids.—Absent.

Esters.—The saponification number was 11.6, representing 4 per cent. of esters, calculated as $C_{12}H_{20}O_2$. In order further to investigate the esters 100 c.c. of the original oil was saponified with 50 c.c. of a 0.5 N. alcoholic solution of sodium hydroxide. After saponification 60 c.c. of water was added to precipitate the oil; the aqueous liquor was separated and evaporated to one-third of its bulk, acidified with hydrochloric acid, and extracted with ether. The ethereal extract was dried over calcium sulphate, and allowed

to evaporate in the air. The acid crystallised in shining laminae, resembling those of benzoic acid. They were recrystallised from ether; melting point 119-120 deg. (M.P. of benzoic acid = 121 deg.) The crystals were only sparingly soluble in water, but were readily so in ammonium hydroxide. A neutral solution of the ammonium salt gave a buff-coloured precipitate with ferric chloride solution. These reactions indicate the presence of a benzoate in the oil; there was not, however, sufficient material to identify the esters further.

Alcohols.—Saponification number after acetylation was 24.9, corresponding to 3.7 per cent. of free alcohols of the formula $C_{10}H_{18}O$.

Phenols.—Shrinkage in volume on treatment with a 5 per cent. solution of sodium hydroxide was nil.

Aldehydes and Ketones.—Absence shown by bisulphite absorption.

Cineole.—The presence of this substance was not indicated by the physical properties of the oil, nor could any trace be detected by Hirsch's delicate iodole test.

Summary.

The oil consists as follows:—

d α -Pinene, 80 to 90 per cent.

Esters (partly benzoates), 4 per cent.

Alcohols, 3.7 per cent.

The oil is interesting as the source of a highly dextrorotatory pinene, but this has at present no technical application which would, taking into account the small yield, make the distillation of the oil in quantity a commercial success.

The author is indebted to Mr. P. R. H. St. John for the introductory botanical characterisation, and for assistance in collecting the leaves and distilling the oil, and to Dr. Green for much helpful advice in the analysis.

Addendum.—A sample of *Eugenia myrtifolia*, another species indigenous to Eastern Australia, was also examined, but although some forty pounds of the foliage were submitted to steam distillation in the usual manner no visible traces of oil were obtained.

PART II.—*The Calculation of the Oil Content of Foliage from Measurements of the Number and Size of the Oil Glands.*

By A. E. DAWKINS, B.Sc.

The collection and distillation of oil-containing materials is often a matter involving much labour. Since therefore the oil is well known to occur in the case of many species in small, well-defined oil-dots or oil-glands, it was thought that it might be possible to forecast the oil content of any particular species by making a few measurements of the size and number of the oil-dots, weight of leaf, etc.

Let $\frac{\pi}{6}d^3$ be the average volume of the glands in *c.c.*,

n the number per sq. c.m.,

g the specific gravity of the oil,

w the weight of leaf per sq. c.m.,

p the ratio of the weight of leaves to the total weight of leaves and stalks as usually taken for distillation.

Then assuming that the oil glands are spherical the percentage yield of oil will be

$$\frac{52.4pd^3ng}{w}$$

The measurement of the size and number of the oil-glands can readily be accomplished microscopically, using an eye-piece provided with suitable micrometer scales.¹

The specific gravity of the oil can of course only be determined when a sample of the oil is available. For most oils, however, a sufficient approximation will be attained by giving g the value of 0.9.

The value p is determined by stripping one or two typical branchlets, and weighing the leaves and the stalks separately.

The accuracy of this method may be judged from the following series of measurements on several species of oil-bearing plants which we have recently had the opportunity of distilling.

¹ A convenient scale for counting the number of oil-dots can be easily made by ruling a series of squares on a thin sheet of mica.

Species.	Nature of leaf.	Oil-glands.		<i>g</i>	<i>w</i>	<i>p</i>	Percentage yield of oil.	
		Mean diam. mms.	<i>n</i> per sq. cm.				calc'd.	realized.
<i>Eucalyptus radiata.</i>	large	.113	1310	.88	.0197	.71	3.06	2.70
	small	.097	1465	-	.0208	-	2.10	
<i>Eucalyptus viminalis.</i>	-	.113	850	.92	.039	.67	1.03	1.32
<i>Eucalyptus kitsoni.</i>	-	.155	227	.91	.032	.76	.95	.85
<i>Leptospermum lanigerum</i>	large	.075	1090	.98	.017	.46	.60	.56
	small	.078	960	-	.013	-	.82	
<i>Eugenia Smithii.</i>	large	.091	475	.86	.033	.82	.44	.36
	small	.072	940	-	.037	-	.33	

The distillations were carried out on fresh material, from a half to three hundred-weights of foliage being used in each case. It will be seen that the agreement is as close as can be expected in view of the difficulty of obtaining a representative sample.

The method and formula may, therefore, be applied to indicate the approximate yield of oil to be expected from any oil-producing plant.

PART III.—*The Essential Oil of Eucalyptus platypus.*

By J. C. EARL, A.I.C.

By courtesy of the Director of the Melbourne Botanic Gardens, a supply of the leaves of *Eucalyptus platypus*, a tree indigenous to Western Australia, was obtained from the Gardens for the purposes of distillation.

The yield of oil obtained on distillation of the fresh leaves was 1 per cent.

The oil had the following constants:—

Specific gravity at 15°/15°	- - - -	0.9045
Optical rotation in 100 mm. tube at 12° C, α_D	- - - -	+ 9.1°
Refractive index at 20° C, n_D	- - - -	1.4675
Saponification number	- - - -	6
Saponification number after acetylation	- - - -	24
Aldehyde and ketone-content determined by absorption with 30 % sodium bisulphite solution	- - - -	nil
Cineole content by direct absorption with 50 % solution of resorcin	- - - -	59 % by weight.

The results of a fractional distillation of 50 c.c. of the oil under atmospheric pressure, and of the examination of the fractions obtained, are given in the following table:—

Fraction.	Temperature.	Volume of oil distilled.	S.G. 15°C/15°C	$\alpha_D^{15^\circ\text{C}}$	$n_D^{11.5^\circ\text{C}}$
A - -	Up to 163.5°C	2.15 c.c.	—	—	—
B - -	163.5°C - 167°C	9.3 c.c.	0.886	+ 20.8°	1.4680
C - -	167 °C - 170°C	10.05 c.c.	0.893	+ 16.1°	1.4673
D - -	170 °C - 175°C	9.55 c.c.	0.903	+ 8.5°	1.4667
E - -	175 °C - 184°C	8.75 c.c.	0.916	+ 0.2°	1.4660
F - -	184 °C - 206°C	2.95 c.c.	0.926	—	1.4692
G - -	206 °C - 240°C	2.85 c.c.	0.937	—	1.4845
H - -	{ Residue boiling } { above 240°C }	4.4 c.c.	0.952	—	1.5040

The low initial boiling temperature combined with the positive rotation of the oil, indicated the probable presence of pinene. In confirmation of this, a crystalline nitroso-chloride of melting point 106° C was prepared from fraction B. Fraction D yielded a small quantity of a crystalline nitrosite which could only be purified by dissolving in chloroform and precipitating with petrol; thus obtained it had a melting point of 104° C. This indicated the presence of a small proportion of phellandrene in the oil. The residue, H, was dissolved in dry ether, and dry hydrochloric acid gas passed through; no crystalline hydrochloride could be isolated from the resulting product.

For further examination of the oil and confirmation of the results of the above preliminary investigation, 200 c.c. of the oil were fractionated at 32 to 34 mm. pressure. The following results were obtained:—

Fraction.	Temperature.	Weight distilled.	S.G. 15°C/15°C	α_D at 19°C
I. - -	Up to 72°C	33.75 gms.	0.879	+ 21.4°
II. - -	72°C - 75°C	53.73 gms.	0.882	+ 15.5°
III. - -	75°C - 79°C	37.70 gms.	0.900	+ 6.7°
IV. - -	79°C - 92°C	27.70 gms.	0.912	- 1.5°
V. - -	Residue + loss	28.02 gms.	0.946	—

Pinene—Fraction I. yielded a nitroso-chloride similar to that previously obtained. The nitrol-piperide prepared from this compound melted at 118-119° C.

Phellandrene.—Fraction II. yielded a small quantity of nitrosite, which after purification melted at 105-106° C. There seems little doubt that this was phellandrene nitrosite.

Cineole (eucalyptol).—The cineole-iodol addition compound, melting at 113° C, after recrystallisation from benzene, was readily obtained from a portion of fraction III.

Aromadendrene.—The residue, V., gave the colour reactions attributed by Baker and Smith to aromadendrene.

Summary.

The following approximate composition may be assigned to the oil:—

Pinene	-	-	-	-	-	20-25%
Phellandrene	-	-	-	-	-	10-15%
Cineole	-	-	-	-	-	55-60%
Aromadendrene	-	-	-	-	-	10-15%
Alcohols, free, and combined as esters,						
up to	-	-	-	-	-	5%

I have to acknowledge my thanks to Professor Masson for encouragement and permission to use the University laboratories, to Dr. Green for many suggestions in the course of the work, and to Mr. St. John for assistance in the distillation of the oil from the leaves.